Structure of Diisopropylammonium Dicitratoborate and Crystallochemical Features of Alkylammonium Complexes with Boric and Citric Acids


Abstract—Single crystals of diisopropylammonium dicitratoborate of the formula (C\(_{3}\)H\(_{7}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} (I) were prepared and characterized by X-ray diffraction. The crystals are monoclinic, space group C2/c, a = 15.9978(5) Å, b = 11.0805(4) Å, c = 13.1872(4) Å, α = 90°, β = 103.34(1)°, γ = 90°, V = 2274.5 (1) Å\(^3\), Z = 8, \(\rho_{\text{calc}} = 1.440\) g/cm\(^3\), 2237 reflections with \(I > 2\sigma(I)\); \(R_I = 0.0408\). Structure I is built from complex spiran-type dicitratoborate anions and diisopropylammonium cations. In the crystal packing, the anions and the cations form staggered stacks linked by a system of hydrogen bonds involving three independent contacts O(N)—H···O. X-ray diffraction data for structure I were compared with those for complexes of boric and citric acids with ammonium and alkylammonium cations.

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In the study of reactions of boric acid with oxygen-containing organic ligands [1, 2], systematic X-ray diffraction investigations are carried out at the Boron Chemistry Laboratory of the Institute of Inorganic Chemistry of the Riga Technical University. The crystal structures of neutral, cationic, and anionic boron complexes (BCs) with aliphatic and aromatic hydroxy acids, dicarboxylic acids, diols, triols, tetrols, etc. have been studied [3]. To find out how cations influence the crystal structures, systematic crystallographic studies of BCs with a single organic ligand are underway. Citric acid is used as the ligand because dicitratoborate salts crystallize more easily. To date, 28 crystal structures of dicarbocenates with singly and doubly charged metal (Li\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), Ag\(^+\), Ca\(^{2+}\), Li\(^2+\), Na\(^2+\), K\(^2+\), Rb\(^2+\), Cs\(^2+\), and Cd\(^{2+}\)) and nitrogen-containing organic cations have been characterized. The latter included mono- and disubstituted (HO-, H\(_2\)N-, and O\(_2\)N-) quinolinium cations and aliphatic monois-, di-, and trialkylammonium cations: (CH\(_{3}\))\(_2\)NH\(_2\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} [4], (CH\(_{3}\))\(_2\)NH\(_2\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} [5], (C\(_{2}\)H\(_{5}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} [6], and (C\(_{2}\)H\(_{5}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} · H\(_2\)O [7]. The study of BCs with amines is of both theoretical and applied interest because they are widely used as fireproofing agents, corrosion-preventive compounds, antioxidants, etc.

The goal of this work was to examine diisopropylammonium dicitratoborate (C\(_{3}\)H\(_{7}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} (I) by X-ray diffraction for revealing the influence of the diisopropylammonium cation on the properties and stability of the complex and compare it with the known structures of methylammonium dicitratoborate (CH\(_{3}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} (II) [4], dimethylammonium dicitratoborate (CH\(_{3}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} (III) [5], diethylammonium dicitratoborate (C\(_{2}\)H\(_{5}\))\(_{2}\)NH\(_{2}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} (IV) [6], triethylammonium dicitratoborate monohydrate (C\(_{2}\)H\(_{5}\))\(_{2}\)NH{[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} · H\(_2\)O (V) [7], and ammonium dicitratoborate dihydrate NH\(_{4}\){[C\(_{6}\)H\(_{6}\)O\(_{7}\)]\(_{2}\)B} · 2H\(_2\)O (VI) [8].

EXPERIMENTAL

Synthesis of complex I. Diisopropylammonium dicitratoborate was prepared by reacting boric and citric acids with diisopropylamine (the molar ratio of the reagents was 1 : 2 : 1) in water as described in [9]. Single crystals of complex I were obtained as follows. Boric acid (1.55 g, 0.025 mol) and recrystallized citric acid (10.52 g, 0.05 mol) were dissolved with heating in distilled water (20 mL). Then diisopropylamine (2.53 g, 0.025 mol) was added. The solution was slowly cooled to allow crystallization and kept at room temperature until single crystals of desired sizes were grown. The crystalline precipitate was washed with water, ethanol, and diethyl ether, and dried in air. The best crystals were used for X-ray diffraction studies.

X-ray diffraction analysis. Experimental material was collected on a Bruker–Nonius KappaCCD automated diffractometer (MoK\(_{\alpha}\) radiation, \(\lambda = 0.71073\) Å, graphite monochromator). The structure was solved by direct methods followed by the Fourier synthesis and refined by the least-squares method in the full-matrix anisotropic approximation (on \(F^2\)) for the nonhydrogen atoms with allowance for the H atoms located experimentally (the H atoms in the protonated
Table 1. Crystallographic parameters and data collection and refinement statistics for structure I

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<td>Empirical formula</td>
<td>C_3H_{14}B_{0.5}O_{7}N_{0.5}</td>
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<td>FW</td>
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<tr>
<td>T, K</td>
<td>293(2)</td>
</tr>
<tr>
<td>Radiation (λ, Å)</td>
<td>MoKα (0.71073)</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell parameters:</td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>15.9978(5)</td>
</tr>
<tr>
<td>b, Å</td>
<td>11.0805(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>13.1872(4)</td>
</tr>
<tr>
<td>β, deg</td>
<td>103.34(1)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>2274.5 (1)</td>
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<td>Z</td>
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<tr>
<td>ρ calc, g/cm³</td>
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<tr>
<td>m, mm⁻¹</td>
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<tr>
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<td>Crystal dimensions, mm</td>
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<tr>
<td>Crystal color</td>
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<td>Scan mode</td>
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<td>2θ max, deg</td>
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<td>Ranges of h, k, and l indices</td>
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<td>-17 &lt; l &lt; 17</td>
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<tr>
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<tr>
<td>Number of independent reflections [R = 0.0210]</td>
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<tr>
<td>Number of reflections with I &gt; 2σ(I)</td>
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<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares method on F²</td>
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<tr>
<td>GOOF</td>
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<tr>
<td>Final R factor [I &gt; 2σ(I)]</td>
<td>R1 = 0.0408, wR2 = 0.0993</td>
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Table 2. Atomic coordinates (×10⁴; ×10³ for the H atoms) and isotropic thermal parameters U_{eq}(Å², ×10³) in complex I

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Note: The letters “a” and “b” are used to designate two crystallographically independent atoms. The population of the positions of the disordered C(1a), C(1b), H(C1a), H(C1b), H(C2a), H(C2b), H(C2c), H(C2d), H(C2e), H(C2f), H(C3a), H(C3b), H(C3c), H(C3d), and H(C3e) atoms is 0.50.